Light Reflection of Cu-sputtering-coated Cotton Fabrics and Effect of Sputtering Time, Acetone Pretreatment and Fabric Structure

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Abstract- The present research aims to vary the additional value on natural textiles by adding new properties with metal nanoscale coatings and evaluate magnetron sputtering coating technology suitability for natural textile coating. The paper describes the process of magnetron sputtering of copper coatings on six types of cotton textile materials. The analysis of the metal coated textile surface was carried out by scanning electron microscope and using a non-contact optical method. The method was based on the measurement of the difference of uncoated and coated fabric surface reflection mechanisms that allow getting a detailed insight in the textile surface changes after metal coating and during its exploitation. The research results demonstrate, that non-contact optical method can be applied to trace the changes of the textile surface relief, texture, trim after metal coating, as well to trace changes in coating evenness and deposited copper amount after exploitation process without the destruction of samples.

Keywords- Copper; Magnetron Sputtering; Cotton; Non-Contact Optical Method

I. INTRODUCTION

Textile materials have intrinsic properties that make them extremely valuable: they are flexible, light weight, strong, soft, etc. Because of this, they are excellent objects for imparting additional functionalities.

The techniques used to functionalize textile surface generally are grouped into two major categories: chemical and physical. Physical techniques are based on the use of non-chemical forces to control the deposition of functional material on the textile surface^[1]. However, this paper describes the physical surface functionalization technique, i.e. magnetron sputtering and evaluation of its application to natural textile coating.

Sputter technologies provide alternative approaches to the functionalization of textiles using metallic, oxide, polymer and composite coatings to achieve various performance properties^[1]. Physical sputtering is a non-thermal vaporization process during which the surface atoms are physically ejected from a solid surface. This momentum transfer takes place from an atomic-sized energetic bombarding particle which is usually a gaseous ion, accelerated from plas ma^[2].

Magnetron sputtering techniques are widely used to deposit different types of coatings, including metallic, polymer and composite coatings on different substrates^[1]. In magnetron sputtering equipment, parallel magnets are placed near the target surface which constrains the motion of secondary electrons ejected by the bombarding ions to the close vicinity of the target surface. The ion current is also increased by an order of magnitude over conventional diode

sputtering systems, resulting in faster deposition rates at lower pressure [1].

In comparison with other deposition techniques, the most important advantage of sputtering is that even the highest melting point materials can be easily sputtered^[1]. Also the thickness of a sputtered film can be easily controlled by fixing the operating parameters and simply adjusting the deposition time^[1]. Nearly all metallic materials can be deposited on textile substrate by sputtering^[1]. In general, metallization is a metal coating process that adds value and improves the functions of textile materials. Textile materials which were modified with different metals have attracted a great deal of attention owing to their potential applications in technology and design fields^[1].

The present paper describes the properties of copper coating depending on fabric structure, sputtering time, pretreatment of textile substrate and post-treatment (washing) of coated textile. The functionalization of textile materials using sputter coating of copper can significantly modify surface properties of the materials. Moreover, the development of modified materials with improved properties will open up new possibilities for the applications of these materials [1]. Scanning electron microscope (SEM) observations clearly revealed a significant difference in surface morphology before and after the application of a copper sputter coating.

Copper is considered to be safe for humans, as demonstrated by the widespread and prolonged use by women of copper intrauterine devices (IUDs)^[3]. Also animal studies have demonstrated that copper fibbers do not possess skin sensitizing properties. These findings are in accordance with the reduced risk of adverse skin reactions associated with copper^[3,4]. In contrast to the low sensitivity of human tissue (skin or other) to copper, micro-organisms are extremely susceptible to copper^[5,6]: copper surface kills over 99.9% of bacteria (Escherichia coli, Enterobacter aerogenes, MRSA, Pseudomonas aeruginosa, Staphylococcus aureus) for 24 hours^[7].

From the published material analysing followed, that the coatings deposited by magnetron sputtering process in exploitation are more sustained than the coatings deposited by vacuum evaporation process, as it is a plasma coating process whereby sputtering material is ejected due to bombardment of ions to the target surface^[1,2].

The results of our previous research evince that copper coating can be deposited on pure cotton textile by magnetron sputtering without destruction of the substrate^[8, 9]. Achieved

during sputtering coating on the cotton textile surface have better resistance to abrasion test than to washing test^[8].

II. MATERIALS AND METHODS

A. Materials

In the present study magnetron sputtering technology was evaluated in terms of the deposition of metal thin films on different cotton textile substrates. During the experiment six types of commercial woven 100% plain weave pure cotton fabrics were subjected to magnetron sputtering:

- cotton fabric with surface density 67.34 g/m² from yarns of linear density 10.4 Tex, the thickness of the fabric 0.24 mm; the measurement was taken by the textile fabric thickness tester "TH-25";
- cotton fabric with surface density 50.91 g/m² from yarns of linear density 8.4 Tex, the thickness of the fabric 0.21 mm:
- cotton fabric with surface density 74.68 g/m² from yarns of linear density 11 Tex, the thickness of the fabric 0.23 mm.
- cotton fabric with surface density 72.82 g/m² from yarns of linear density 8.2 Tex, the thickness of the fabric 0.28 mm:
- 5) cotton fabric with surface density 110.04 g/m² from yarns of linear density 11.2 Tex, the thickness of the fabric 0.24 mm.
- cotton fabric with surface density 68.15 g/m² from yarns of linear density 9.8 Tex, the thickness of the fabric 0.25 mm.

B. Surface Preparation before Textile Coating

To provide good interfacial contact between the fibre surface and the deposited metal, cotton fabric samples were washed at temperature 90°C with detergent without optical brighteners. Nevertheless, the washing did not remove all the oil. As a result about half of washed samples were immersed in 80% acetone solution at room temperature for 5 minutes¹¹⁰, and were washed twice with distilled water. Drying was carried out on a horizontal surface.

C. Magnetron Sputtering Technology

Magnetron sputtering is a plasma coating process during which sputtering material is ejected due to the bombardment of ions to the target surface. The vacuum chamber of the coating machine is filled with inert gas argon (argon amount during sputtering time for all samples was approximately 2.5 cm³). By applying a high voltage (~700V), a glow discharge was created, resulting in the acceleration of ions to the target surface and to the plasma coating. The argon-ions ejected sputtering materials from the target surface, resulting in a deposited coating layer on the products in front of the target. In the vacuum chamber seven fabric samples were fixed on the rotating disk, disk rotation rate was 20 min⁻¹ and during sputtering time (60 seconds) sputtering time for each sample surface was 0.63 seconds. Physical vapour deposition, especially sputtering technology, has been regarded as an environmentally friendly technique for the functionalization of textile materials^[1].

D. Non-contact Optical Method of Surface Examination

Diffuse light reflection is inherent for woven plain weave cotton fabrics, due to the geometry of its surface (relief, texture). Most of the metals reflected well incident, visible light rays. The non-contact optical method hypothesis is based on the difference between the uncoated and the coated fabric

surface light reflection mechanisms. Those mechanisms provide new opportunities to understand the changes in textile material surface structure and deposited coatings. In order to get a detailed insight into the textile surface changes after the, application and the exploitation of metal coating, as well as to develop a tool for comparative analysis, the surfaces of the samples were examined with the non-contact optical method. In order to measure the intensity of the reflected light "He-Ne" laser with wavelength 628.3 nm was used. The measurements of the reflected light intensity were obtained with a photo diode. The value of the light reflection intensity was displayed on the "Solo PE Gentec-E" laser power and energy meter. The angle between the incident and the reflected angles varied from -70° to 70° with a step 5°. After the copper deposition, the reflected light intensity was measured in five different surface spots for each sample prepared corresponding to the deposition time and pretreatment. The average values of measurements for every sample group before and after washing tests were calculated and presented in graphs for each deposition time.

The method of reflected light intensity measurement is based on a Lambert's cosine law: if the solid is reflected uniformly in all directions, the radiation intensity of the wave of a given direction (I_{β}) must be proportional to the cosine of the angle β and the incident beam intensity (I_{0}) (1). An important illation of Lambert's cosine law is that the surface reflects the same level of radiance even when viewed from different angles.

$$I_{\beta} = I_0 \cos \beta \tag{1}$$

Taking into account that natural fibres and surfaces of textile materials had diffuse light reflection, and surface roughness partially even up after metal deposition process, as well as other surface properties changes occurred. The comparison of measurements of light reflection intensities of textile samples with different pre-treatments, coating technologies and after exploitation process, gives the opportunity to receive information about changes of textile surface properties, including structure changes [4].

$\ensuremath{\mathrm{III}}$. RESULTS AND DISCUSSION

For experiment two sample groups with acetone solution pre-treatment and without acetone solution pre-treatment were prepared. Each group consisted of 54 samples, divided in smaller groups according to sputtering time duration and cotton textile type (Table I).

TABLE I SAMPLE GROUPS PREPARED FOR EXPERIMENT

	Sputtering Time		
Sample Groups	20 seconds	40 seconds	60 seconds
	Without Pre-ti	reatment	
Fabric 1	3	3	3
Fabric 2	3	3	3
Fabric 3	3	3	3
Fabric 4	3	3	3
Fabric 5	3	3	3
Fabric 6	3	3	3
			Total: 54
Wi	ith Acetone Solutio	n Pre-treatment	
Fabric 1 A	3	3	3
Fabric 2 A	3	3	3
Fabric 3 A	3	3	3
Fabric 4 A	3	3	3
Fabric 5 A	3	3	3
Fabric 6 A	3	3	3
		•	Total: 54
			Total: 108

A. SEM Micrographs Analysis

The morphological changes of the natural textile as a result of coating with copper and after its washing have been investigated using SEM (Tescan, Mira//LMU Schottky).

Copper coating can be deposited on cotton textile by magnetron sputtering technology without destruction of substrate from natural fibres (Fig. 1 - Fig. 6). SEM micrographs (Fig. 1 - Fig. 6) evince that the copper coating is not a flat film on the cotton textile surface, thus copper particles are deposited on fibres without changing the textile surface structure.

SEM micrograph (Fig. 1 - Fig. 6) illustrates that copper coatings deposited with magnetron sputtering technology on the cotton textile materials are mostly without defects, distributed evenly not only on the surface of yarns but in depth of textile material as well. The quality of the textile substrate insignificantly influenced the quality of sputtered coatings; on the samples from materials Fabric 1 (Fig. 1) and Fabric 6 (Fig. 2) some insignificant micro defects can be observed.

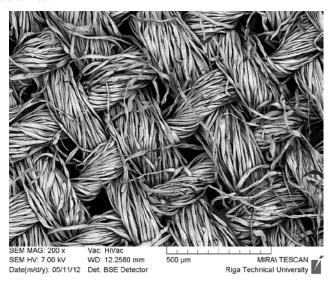


Fig. 1 Cotton Fabric 1, magnet ron sputtering time 60 seconds

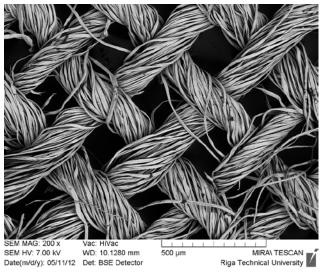


Fig. 2 Cotton Fabric 2, magnet ron sputtering time 40 seconds

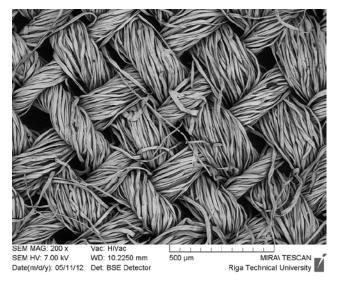


Fig. 3 Cotton Fabric 3 A, with acetone solution pre-treatment 5 minutes, magnetron sputtering time 60 seconds

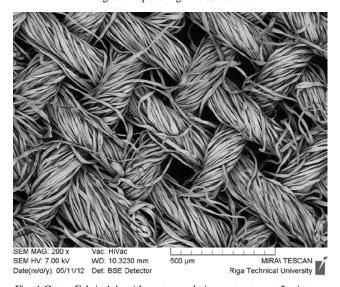


Fig. 4 Cotton Fabric 4 A, with acetone solution pre-treatment 5 minutes, magnetron sputtering time 40 seconds

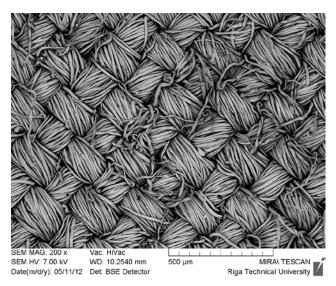


Fig. 5 Cotton Fabric 5, magnet ron sputtering time 20 seconds

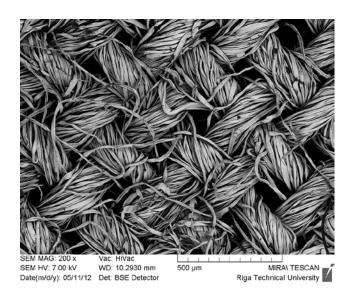


Fig. 6 Cotton Fabric 6, magnet ron sputtering time 40 seconds

The maximal thickness of copper coating on the glass substrates have been measured using SEM. The copper coating with maximal thickness deposited during total sputtering time 20 seconds (for each sample 0,21 seconds) is approximately - 30 nm, 40 seconds (for each sample 0,42 seconds) is approximately - 60 nm and 60 seconds (for each sample 0,63 seconds) is approximately - 90 nm for each of seven fabric samples fixed on the rotating disk (rotation 20 min⁻¹). The deposited copper coating thickness has the straight-line correlation with sputtering time from 20 to 60 seconds (Fig. 7).

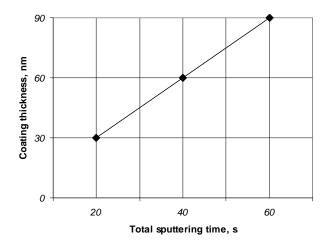


Fig. 7 Correlation between sputtering time and coating thickness

In order to evaluate the impact of the exploitation on copper coating washing test was carried out. Samples from all sputtering time groups were washed at temperature 30°C with detergent without optical brighteners, then the drying step was carried out at a horizontal surface.

SEM micrographs (Fig. 8 - Fig. 13) show changes of copper coating on cotton textile surface after the washing test. The coatings were obtained during sputtering time 20, 40 and 60 seconds with and without pre-treatment in acetone solution. The micrographs of samples with sputtering time 20 seconds (Fig. 8 - Fig. 9) evince that approximately 70% of copper coating disappeared from the sample surfaces.

The micrographs of samples with sputtering time 40 seconds (Fig. 10 - Fig. 11) evince that approximately 50% of copper coating disappeared from the samples surfaces.

The micrographs of samples with sputtering time 60 seconds (Fig. 12 - Fig. 13) evince that approximately 15% of copper coating disappeared from samples surfaces. At the same time, approximately 85% of copper coating remained on the surface of the samples.

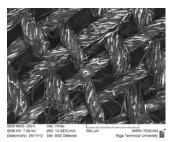


Fig. 8 Cotton Fabric 1 sample, magnetron sputtering time 20 seconds

Fig. 9 Cotton Fabric 2 A, magnetron sputtering time 20 seconds

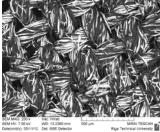
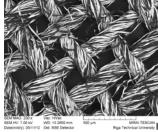


Fig. 10 Cotton Fabric 3, magnet ron sputtering time 40 seconds

Fig. 11 Cotton Fabric 4 A, magnetron sputtering time 40 seconds



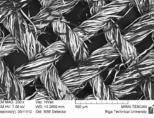


Fig. 12 Cotton Fabric 5, magnetron sputtering time 60 seconds

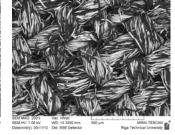


Fig. 13 Cotton Fabric 6 A, magnetron sputtering time 60 seconds

B. Non-contact Optical Method of Surface Examination

The measurements of the reflected light intensity represent changes on the textile surface as a result of metal deposition and textile exploitation. For each sample 120 measurements (5 spots and 24 angles) were taken before and after the washing test, the obtained measurements show changes on sample surface reflective properties as the result of its coating with copper and exploitation process.

The statistical dispersion of the measurements' of reflected light intensity is approximately $\sigma = 0$, 41. The dispersion value can be explained with uneven surface structure and big porosity of woven cotton textile surface.

From the graph represented in Fig. 14, a conclusion can be drawn that experimental light reflection curve (reflected light intensity of coated with copper textile) in comparison with

uncoated textile experimental light reflection curve still has diffuse reflection. It is implied that the deposited copper coating on textile surface repeats textile material surface structures. The sample with the deposited copper coating has a notable deviation from the diffuse reflection that can be explained by the fact that the copper coating absorbed the part of incident light, as well as the textile surface after coating became evener.

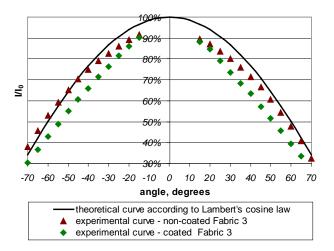


Fig. 14 Theoretical diffuse reflection curve in comparison with experimentally received reflection curves, (I/I₀ - beam intensity level, rationed to the maximum)

The graphs represented in Fig. 15 - Fig. 17 demonstrate the changes in samples depending on sputtering time; it was observed that with a longer sputtering time reflectance is increased. It confirms that the amount of copper on the surface of textile increases with greater sputtering time, whereas the high reflectance of non-coated textile can be explained by white sample colour.

In this study, it was investigated integrated ability of light reflection of the coated sample surface interconnectedness with sputtering time. The graph represented in Fig. 15 illustrate that the sputtering time has straight-line correlation with the light reflection intensity. As was mentioned above the thickness of the deposited copper coating has the straight-line correlation with sputtering time from 20 to 60 seconds, so a conclusion can be drawn that coating thickness has the straight-line correlation with light reflection intensity.

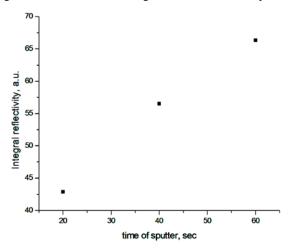
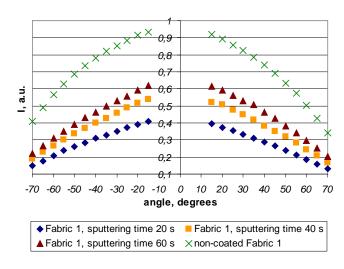


Fig. 15 Processing time influences on light reflection (arbitrary units – intensity level rationed to the maximum)

The graphs represented in Fig. 16 (a, b) prove that the type of the textile material has an impact on the reflected light intensity of samples, but not influences relation of the reflected intensity of samples with different sputtering time. It can be explained with the equal deposited copper amount on the sample surface from different types of cotton textiles.

The reflected light intensity (Fig. 16 a, b) rapidly increased with increasing of sputtering time at sputtering time 40 seconds and for 1,5 time exceeded the relevant indicator obtained by the samples with sputtering time 20 seconds. It can be explained with increasing of sputtered copper coating thickness and wherewith increasing reflection of mirror light.



a

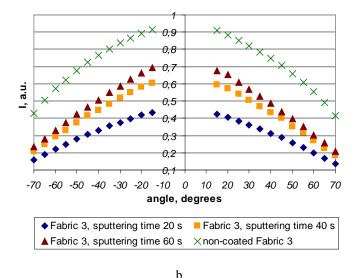
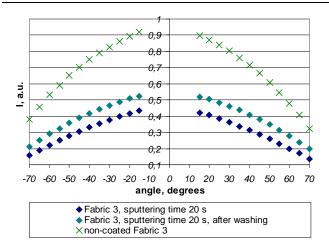


Fig. 16 Processing time and Fabric 1 and 3 structure influences on light reflection

After the washing test, the textile material type has an impact on the reflected light intensity of samples coated with sputtering time 20 seconds as illustrated in Fig. 17 (a, b). It can be explained with the fact that approximately 70% of copper coating disappeared from the surface of the cotton textile samples that can be observed in micrographs (Fig. 7 - Fig. 8).



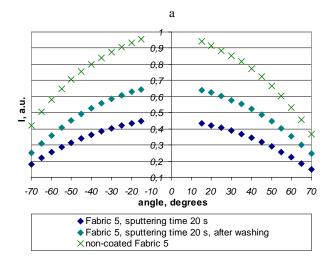
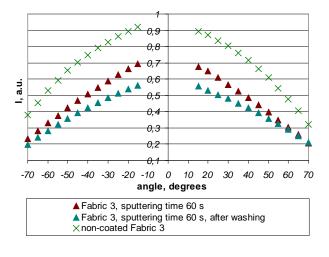
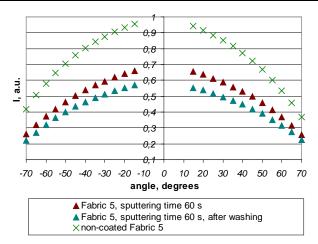


Fig. 17 Washing and Fabric 3 and 5 structure effects on copper covered cotton fabric surface light reflection (deposition time 20 s)

The graphs represented in Fig. 18 (a, b) demonstrate that after the washing test of samples coated with sputtering time 60 seconds the relation between the reflected light intensity before and after washing for all types of material are equal. It can be explained with the fact that about 85% of copper coating still remained on the surface of the cotton textile samples.

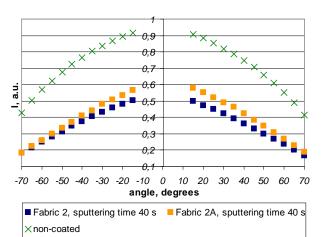


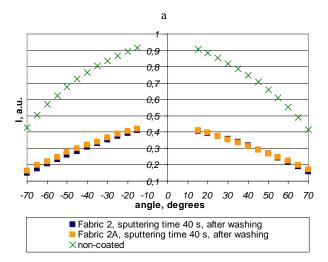


h

Fig. 18 Washing and Fabric 3 and 5 structure effects on copper covered cotton fabric surface light reflection (deposition time 60 s)

The graph (Fig. 19 a) demonstrates changes in reflected light intensity of the coated samples depending on the use of the acetone solution pre-treatment before sputtering. It is evident that the cases with acetone solution pre-treatment increased reflected light intensity in comparison with samples without acetone solution pre-treatment. It can be explained with increasing of copper amount on the surface of the textile.





h

Fig. 19 Acetone solution pre-treatment and washing influences on copper coated Fabric 2 surface light reflection (deposition time 40 s)

As shown in the graph (Fig. 19 b) the reflected light intensity of both samples after the washing test reached almost the same level. It is intrinsic for all types of cotton textiles used in this experiment and can be explained with the fact that after the washing test approximately the same copper amount remained on both samples with acetone solution pretreatment and without it.

IV. CONCLUSIONS

The influence of the pre-treatment and post-treatment on the amount of copper deposited by sputtering on the textile surface is under investigation. Copper coating can be deposited on pure cotton textile by magnetron sputtering technology with rotating disk not destroying the substrate made of natural fibers, the typical textile properties (softness, flexibility etc.) and surface relief and texture were not influenced.

The reflected light measurements and SEM micrographs evince that copper coating is not a flat film on the cotton textile surface, thus, the copper particles deposited at fibers and textile have not changed their surface relief, texture, trim.

The measurements of the reflected light intensity, the comparative analyses and SEM micrographs show, that the sputtering time 20 seconds with disk rotation 20 min⁻¹ are enough to obtain even copper coating on cotton textile surface, 20 seconds long sputtering allows to achieve copper coating, which is distributed evenly not only on the surface of yarns but in depth of textile material as well.

The washing test results show that coating received after sputtering time 20 seconds has the worst stability and adhesion in comparison with 40 seconds and 60 seconds sputtering time. Whereas the best coating stability is achieved with sputtering time 60 seconds (disk rotation 20 min⁻¹).

The measurements of the reflected light could be used to trace the metal coating changes depending on the impact of exploitation.

ACKNOWLEDGMENTS

This work has been supported by the European Social Fund within the project support for the implementation of doctoral studies at Riga Technical University.

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